Comments on the calculation for the specific heat in the Debye model

Markus Deserno, April 15, 2020

During the lecture the question came up how to properly define the wave vectors in the Debye solid calculation. Is it $\frac{\pi}{L}$ times an integer, or $\frac{2\pi}{L}$ times an integer? I mumbled about "octants" and "proper number of states", but as Keegan pointed out, the spacing of wave vectors in Fourier space should be $\frac{2\pi}{L}$, irrespective of what we think about the total number of modes we wish to include.

In these notes I briefly show, how we can make the $\frac{2\pi}{L}$ case work out consistently.

First, recall that our dispersion relation (in one dimension) was

$$\omega(k) \;=\; 2\tilde{\omega}\left|\sin\frac{ka}{2}\right| \;\stackrel{ka\ll 1}{\approx}\; \tilde{\omega}|ka| \;=\; v|k| \;, \tag{1}$$

where v is the phase velocity. We plotted this in the first Brillouin zone, which ranged from $k = -\frac{\pi}{a}$ to $k = +\frac{\pi}{a}$.

Let us first make sure we understand the spacing of modes. With N particles in one dimension, we need N modes. The width of our Brillouin zone is $\frac{2\pi}{a}$, and so the spacing of individual wave vectors along that line is $\frac{2\pi}{a}/N = \frac{2\pi}{L}$ since $N = L/a$.

So far, so good. But there's a slight complication we should be clear about: each mode has a *complex* amplitude, and that gives it two degrees of freedom. Doesn't that double the number of independent modes? No, because the Fourier amplitudes satisfy $\tilde{x}_{-k} = \tilde{x}_k^*$, and so the mode amplitudes at negative k vectors are fully specified if we know the ones at positive k vectors. More precisely, we can indeed restrict to non-negative wave numbers and find the following modes:

$$\left.\begin{array}{c}1\text{ mode}\\ 2\text{ modes}\\ 1\text{ mode}\end{array}\right\}\quad\text{for}\quad\left\{\begin{array}{l}n=0\\ n\in\{1,2,\dots,\frac{N}{2}-1\}\\ n=\frac{N}{2}\end{array}\right. \quad . \tag{2}$$

Check that these are indeed N modes. Alternatively, we can take the lazy view that there is one real amplitude per wave vector, but also count all the amplitudes at negative wave vectors. We then get exactly one mode for each of the following numbers:

$$n \in \left\{-\frac{N}{2}+1, -\frac{N}{2}+2, \dots, -2, -1, 0, 1, 2, \dots, \frac{N}{2}-1, \frac{N}{2}\right\} . \tag{3}$$

Observe that this will also give us exactly N modes. Even more importantly, we realize that in *both* cases the minimal spacing between different wave vectors is 1 in n-space and $\frac{2\pi}{L}$ in k space. So: same spacing, same numbers, different degeneracies.

Since the second way of counting is technically easier, we will use it now.

Let's upgrade to three dimensions and adopt Debye's suggestion of (1) restricting to the linear piece of the dispersion relation, $\omega(k) = v|k|$, (2) a spherical Brillouin zone in $\vec{k}$-space of radius k_D that (3) contains exactly $3N$ modes. To calculate their number, we sum them up or, more easily, *integrate* them up by first smearing out the delta-peaks. Since the spacing of modes along each dimension is $2\pi/L$, the volume in three-dimensional $\vec{k}$-space belonging to each delta-peak is $(2\pi/L)^3$, and hence the *density of states* in $\vec{k}$-space is $1/(2\pi/L)^3 = (L/2\pi)^3$. But this is a constant, and so the volume integral over the density is just the density times the volume:

$$3\int_{|\vec{k}|<k_\mathsf{D}} \mathsf{d}^3k \, \left(\frac{L}{2\pi}\right)^3 = 3\times\left(\frac{L}{2\pi}\right)^3 \times \frac{4\pi}{3}k_\mathsf{D}^3 \; . \tag{4}$$

Demanding that this equals $3N$ leads to

$$k_\mathsf{D} = \left(\frac{6\pi^2 N}{L^3}\right)^{1/3} \; . \tag{5}$$

We can now calculate the average energy by multiplying the density of states in $\vec{k}$-space by the average energy per mode and integrating over the Debye sphere:

$$U = 3\,\left(\frac{L}{2\pi}\right)^3 \int_{|\vec{k}|<k_\mathsf{D}} \mathsf{d}^3k \, \frac{\hbar v|\vec{k}|}{\mathsf{e}^{\beta\hbar v|\vec{k}|}-1} = 3\,\left(\frac{L}{2\pi}\right)^3 \int_0^{k_\mathsf{D}} \mathsf{d}k \; 4\pi k^2 \, \frac{\hbar v k}{\mathsf{e}^{\beta\hbar v k}-1} \; . \tag{6}$$

Using the substitution $x := \beta\hbar v k$, and hence $\mathsf{d}x = \beta\hbar v\,\mathsf{d}k$, we get

$$\begin{aligned} U &= 12\pi\,\left(\frac{L}{2\pi}\right)^3 \frac{1}{\beta(\beta\hbar v)^3}\int_0^{\beta\hbar v k_\mathsf{D}} \mathsf{d}x\,\frac{x^3}{\mathsf{e}^x-1} \\ &\overset{T\to 0}{\sim} 12\pi\,\left(\frac{L}{2\pi}\right)^3 \frac{1}{\beta(\beta\hbar v)^3}\frac{\pi^4}{15} = L^3\frac{3\pi^2}{30(\hbar v)^3}(k_\mathsf{B}T)^4 \; . \end{aligned} \tag{7}$$

This is the result we also derived in the lecture, on conceivably more dubious grounds. You can easily verify that the $T\to\infty$ asymptotics also checks out, giving $3Nk_\mathsf{B}T$.

As a final comment: in three dimensions we claimed that we just get more modes, but we can re-use the dispersion relation derived in one dimension. That is of course not actually true. Specifically, there is no reason to believe that the transverse and the longitudinal modes have the same dispersion relation. However, it turns out that both of them are still linear at small k and so the only *relevant* difference is that the phase velocities for these two classes of modes are different, let's call them $v_\perp$ for the transverse modes and $v_{||}$ for the longitudinal ones. This then leads to the following fairly obvious generalization of our result:

$$u = \frac{U}{V} = \frac{\pi^2}{30\,\hbar^3}\left(\frac{2}{v_\perp^3}+\frac{1}{v_{||}^3}\right)(k_\mathsf{B}T)^4 \; . \tag{8}$$